

CHARACTERIZATION OF CALCIUM OXIDE PREPARED BY HYDRATION-DEHYDRATION METHOD

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To my beloved mother and father
Thank you for your support and courage

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ABSTRACT

Calcium oxide, CaO is an important inorganic catalyst, used in toxic waste remediation agent and adsorbent. In this study, CaO was prepared by hydration-dehydration method using commercial calcium oxide as starting material, converted into its hydroxide by sonicating it in ultrasonic water bath for one hour, then, undergone dehydration step by heating under high vacuum at different temperatures which were 200, 300, 400, 500, 600, 700 and 800°C respectively. The prepared samples were characterized using several techniques including Thermal Gravimetry Analysis (TGA), Fourier Transform Infrared (FT-IR), X-Ray Diffraction (XRD), Nitrogen Gas Adsorption (NA) and Field Emission Scanning Electron Microscope (FESEM). The FT-IR shows that the elimination of hydroxide and carbonate species increased with the increasing calcination temperature. By XRD, the prepared CaO-700 shows the smallest particle size which is 27.93 nm compared to commercial CaO with particle size of 37.14 nm. The basicity study of the prepared CaO carried out using back titration method showed that the prepared CaO-800 was found to be very high basic which is 1.78 mmol/g. The result obtained using Electron Spin Resonance spectroscopy to the CaO-800 irradiation by UV in H₂, showed that the cavity of CaO-800 was too large to trap electrons, containing several impurities such as manganese, Mn²⁺ that might inhibit the formation of trapped electron in CaO.

ABSTRAK

Kalsium oksida, CaO merupakan mungkin bukan organik yang penting, digunakan sebagai bahan perawat sisa toksik dan bahan penjerap. Dalam kajian ini, CaO disediakan melalui kaedah penghidratan-penyahhidratan menggunakan kalsium oksida komersial sebagai bahan pemula yang kemudian ditukarkan kepada kalsium hidroksida melalui aliran gelombang bunyi di dalam rendaman air selama satu jam. Seterusnya, proses penyahhidratan kalsium hidroksida yang terhasil dijalankan melalui pemanasan pada pelbagai suhu iaitu 200, 300, 400, 500, 600, 700 dan 800°C menggunakan vakuum berkuasa tinggi. Pencirian sampel dilakukan menggunakan kaedah pencirian Pemeteran Gravitasi Haba, Spektroskopi Inframerah, Pembelauan Sinar-X, penjerapan nitrogen dan Mikroskop Imbasan Elektron. Spektroskopi inframerah menunjukkan penyingkiran molekul hidroksida dan karbonat meningkat dengan peningkatan suhu pemanasan. Analisis menggunakan pembelauan sinar-X menunjukkan sampel CaO-700 menghasilkan saiz partikel paling kecil, iaitu 27.93 nm berbanding CaO komersial dengan saiz partikel 37.14 nm. Keputusan ujian bes melalui kaedah pentitratan semula menunjukkan sampel CaO-800 paling berbes iaitu 1.78 mmol/g. Keputusan dari Resonans Spin Elektron ke atas sampel CaO-800 yang dikenakan sinaran UV dan dialirkan dengan gas hidrogen menunjukkan rongga yang terbentuk adalah terlalu besar untuk memerangkap elektron. Tambahan pula terdapat bendasing mangan, Mn, yang menghalang pemerangkapan elektron pada CaO.

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LIST OF ABBREVIATIONS

CaO	-	Calcium oxide
Ca(OH) ₂	-	Calcium hydroxide
ESR		Electron Spin Resonance
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared
HCl	-	Hydrochloric acid
H ₂	-	Hydrogen
ICSD	-	Inorganic Crystal Structure Database
KBr	-	Potassium bromide
Mn	-	Manganese
NaOH	-	Sodium hydroxide
nm	-	Nanometer
TGA	-	Thermogravimetric analysis
UV	-	Ultra violet
XRD	-	X-Ray Powder Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background of the research

Recently, metal oxides have undergone rapid technological and commercial interest due to their important role in corrosion protection, catalysis, sensors, fuel cells and ceramics. In the catalysis industry, alkaline earth metal oxide is one of the most well-researched catalysts. Alkaline earth metal oxide such as MgO, CaO and BaO have displayed a highly active catalysis for certain base-catalyzed reaction such hydrogenation, nitroaldol reaction and transesterification (Koper, *et al.*, 1997).

Base-catalyzed reaction can be identified as chemical reaction that occurs when the reactants act as acid toward catalyst that act as a base. Certain metal oxides with a single component were found to act as solid base catalysts in the absence of such alkali metals as Na and K. The material may be called solid base catalyst only if it acts as a base toward the reaction by donating an electron pair (Lewis base) or abstraction of proton (Bronsted base) to form anionic intermediates that will undergo catalytic cycles. Alkaline earth metal oxides have shown their potentials as base catalyst due to its properties which can abstract H^+ from reactants or hydrogen gas or can donate electron pair for starting the reactions (Hattori, 2001).

On the other hand, alkaline earth metal oxides possess highly reactive sites. Highly reactive sites will form the basic site or acidic site of the catalyst (Hattori, 2001). Generally, the reactive sites of the metal oxides depend on their surface

defects. The preparation method and activation procedures will be the factors in determining surface concentration and reactivity of such sites. Besides that, the pathway of electron to move from oxide surface to the adsorbed molecules is also important in order to determine the reactive sites. The pathway of consequence reaction strongly depends on the particular surface sites available, also on the nature of the adsorbing molecule.

Physical and chemical characteristics of the prepared metal oxides depend on their preparation methods. Alkaline earth metal oxides are generally prepared by thermal decomposition of alkaline earth metal compounds such as hydroxides, chlorides, sulfates and carbonates. Thermal decomposition of hydroxides and carbonates in air or under vacuum is the most general methodology used to prepare alkaline earth metal oxides as basic catalyst. Decomposition of hydroxide is frequently used to prepare MgO and CaO, whereas BaO and SrO are prepared from the corresponding carbonates as precursor salt (Corma and Iborra, 2006).

The study in catalysis is also related to nanotechnology. Catalysis has been the traditional field of surface chemistry. Due to the initiation of nanotechnology, the control of material on molecular scale at surface becomes more important. The nanosize scale approximately 1 to 100 nm is important in developing nanostructured catalyst. Nano-scale particles with high surface area yield a number of defect sites. The most common defects are coordinatively unsaturated ions arising from edge, corners, anion/cation vacancies and electron excess center (Kolansiski, 2008). Besides that, confinement effects can completely alter the chemical characteristics of sufficiently small nanoparticles. Researchers have also shown that the atomic characteristics of metallic nanoparticles, including particle size and surface composition, are critical to catalytic activity and selectivity.

In this research, hydration-dehydration method assisted with ultrasonic treatment was used in order to create nano-CaO with high surface area and high basicity thus increased its catalytic performance. Hydration-dehydration method was conducted to prepare CaO at various temperatures under vacuum atmosphere. The

correlation between basicity and temperature calcinations during preparation was studied.

1.2 Statement of Problem

In industry, transesterification of palm oil to biodiesel utilizes homogeneous base catalysts such sodium and potassium hydroxide (NaOH and KOH) dissolve in methanol which is a corrosive liquid. However, this process is time consuming and involves expensive separation step. This process is also a non-environmental friendly because implies the consumption of large amount of water for wet washing to remove the salt produced from neutralization process and the residual acid or base catalyst.

The utilization of a successful heterogeneous solid base catalyst will manage most of the economical and environmental drawbacks of a homogeneous process. Heterogeneous catalysts are non-corrosive and environmental friendly. They are also much easier to be separated from liquid products, and can be designed to give higher activity, more selectivity and longer catalyst lifetime. This study used calcium oxide, CaO which is a base catalyst from alkaline earth metal oxide to prepare materials with high surface areas and higher basicity to improve the catalytic properties of these materials thus overcome the drawbacks of homogeneous catalysts in industry.

1.3 Objective of Study

The objectives of this research were to investigate the characteristics and also to study the basicity of prepared CaO. This research's aims are divided into three:

- 1) To prepare CaO from commercial CaO by sonicating and thermal decomposition at various temperatures by using vacuum and pump system.

- 2) To characterize and study the basicity of all prepared CaO.
- 3) To compare the characteristics between commercial, hydrated and the prepared CaO.

1.4 Scope of Study

The scope of the research was to prepare and characterize physico-chemical properties of prepared CaO. This study used commercial CaO as precursor that was sonicated by using ultrasonic water and was undergone thermal decomposition/activation known as dehydration method at various temperatures, 200°C to 800°C using vacuum line system.

The characterization of prepared CaO was done using Thermogravimetry Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Single Point Surface Area- nitrogen adsorption and Field Emission Scanning Electron Microscopy (FESEM). The basicity test was also conducted via back titration method and further strengthens by using ESR.

1.5 Significance of Study

As we know, metal oxide is widely used as catalyst especially in biodiesel production. This study was carried out one of metal oxides that also used as catalyst which is calcium oxide. Commercial calcium oxide was synthesized to produce high surface area and high basicity of calcium oxide that can be used and applied in catalysis industry.

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